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1. I am a citizen of Japan residing at 24-5, Mejirodai 4-chome, Hachioji-shi, Tokyo, Japan.

2. To the best of my ability, I translated

Japanese Patent Application No. 10-193662

from Japanese into English and the attached document is a true and accurate English translation thereof.

3. I further declare that all statements made herein are true, and that all statements made on information and belief are believed to be true; and further that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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Ikuzo Tanaka

Ikuzo Tanaka

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【発明者】

【住所又は居所】 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内

【氏名】 高見 崇

【発明者】

【住所又は居所】 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内

【氏名】 久保田 裕

【発明者】

【住所又は居所】 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内

【氏名】 緒方 安伸

【特許出願人】

【識別番号】 000005083

【氏名又は名称】 日立金属株式会社

【代表者】 枝 徹也

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FERRITE MAGNET AND METHOD FOR PRODUCING SAME

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**Inventor**

Address                  c/o Magnetic Materials Research Laboratory,  
Hitachi Metals, Ltd.  
5200, Mikajiri, Kumagaya-shi, Saitama-ken  
Name                    Tadashi Takami

**Inventor**

Address                  c/o Magnetic Materials Research Laboratory,  
Hitachi Metals, Ltd.  
5200, Mikajiri, Kumagaya-shi, Saitama-ken  
Name                    Yutaka Kubota

**Inventor**

Address                  c/o Magnetic Materials Research Laboratory,  
Hitachi Metals, Ltd.  
5200, Mikajiri, Kumagaya-shi, Saitama-ken  
Name                    Yasunobu Ogata

**Applicant**

Identification No.    000005083

Name HITACHI METALS, LTD.

Representative Tetsuya Eda

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**Attached Papers**

Specification one

Drawings one

ABSTRACT one

## SPECIFICATION

### Title of the Invention

FERRITE MAGNET AND METHOD FOR PRODUCING SAME

### 5 Claims

1. A ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rare earth

10 elements including Y, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$0.01 \leq x \leq 0.4,$

$[x/(2.6n)] \leq y \leq [x/(1.6n)],$  and

15  $5 \leq n \leq 6,$

said ferrite magnet substantially having a magnetoplumbite-type crystal structure.

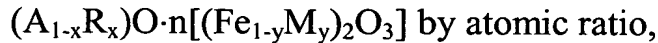
2. The ferrite magnet according to claim 1, further comprising  
0.05-0.5 weight % of  $SiO_2$  and 0.35-0.85 weight % of CaO per said basic  
20 composition.

3. The ferrite magnet according to claim 1 or 2, wherein the distribution of said R element is much more in crystal grain boundaries than in said magnetoplumbite-type crystal grains.

4. The ferrite magnet according to claim 1 or 2, wherein the  
25 distribution of said R element is much more in said magnetoplumbite-type

crystal grains than in crystal grain boundaries.

5. A ferrite magnet having a basic composition represented by the following general formula:



5 wherein A is at least one of Sr and Ba, R is at least one of rare earth elements including Y, at least one element selected from the group consisting of Nd, Pr and Ce being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following conditions:

$$10 \quad 0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

said ferrite magnet substantially having a magnetoplumbite-type crystal structure.

15 6. The ferrite magnet according to claim 5, further comprising 0.05-0.5 weight % of SiO<sub>2</sub> and 0.35-0.85 weight % of CaO per said basic composition.

7. The ferrite magnet according to claim 5 or 6, wherein the distribution of said R element is much more in crystal grain boundaries  
20 than in said magnetoplumbite-type crystal grains.

8. The ferrite magnet according to claim 5 or 6, wherein the distribution of said R element is much more in said magnetoplumbite-type crystal grains than in crystal grain boundaries.

9. A ferrite magnet having a basic composition represented by the  
25 following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,  $R = \frac{1}{2}$   
 wherein A is at least one of Sr and Ba, R is at least one of rare earth  
 elements including Y, at least one element selected from the group  
consisting of La, Nd, Pr and Ce being an indispensable element, M is at  
 5 least two elements selected from the group consisting of Mn, Co, Ni and Zn,  
 and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

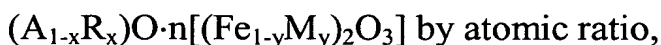
10 said ferrite magnet substantially having a magnetoplumbite-type crystal  
 structure.

10. The ferrite magnet according to claim 9, further comprising  
 0.05-0.5 weight % of  $SiO_2$  and 0.35-0.85 weight % of CaO per said basic  
 composition.

15 11. The ferrite magnet according to claim 9 or 10, wherein the  
 distribution of said R element is much more in crystal grain boundaries  
 than in said magnetoplumbite-type crystal grains.

12. The ferrite magnet according to claim 9 or 10, wherein the  
 distribution of said R element is much more in said magnetoplumbite-type  
 20 crystal grains than in crystal grain boundaries.

13. A method for producing a ferrite magnet having a basic  
 composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one of rare earth  
 25 elements including Y, La being an indispensable element, M is at least one



element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

said method comprising the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu\text{m}$  and said basic composition successively to drying or concentrating, milling, molding in a magnetic field and sintering.

14. The method producing a ferrite magnet according to claim 13, said method comprising the steps of subjecting a raw material powder having said basic composition at the time of calcination step to wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling, molding in a magnetic field and sintering.

15. The method producing a ferrite magnet according to claim 13, said method comprising the steps of subjecting a raw material powder adjusting to said basic composition at the time of wet-fine pulverizing step to wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling, molding in a magnetic field and sintering.

16. The method producing a ferrite magnet according to claim 14 or 15, wherein 0.2-2.0 weight % of a dispersant per a solid component is added at the time of pulverizing or milling.

17. A method for producing a ferrite magnet having a basic

composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rear earth

elements including Y, at least one element selected from the group

5 consisting of Nd, Pr and Ce being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and

x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

10  $5 \leq n \leq 6,$

said method comprising the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu\text{m}$  and said basic composition successively to drying or concentrating, milling, molding in a magnetic field and sintering.

15 18. The method producing a ferrite magnet according to claim 17, said method comprising the steps of subjecting a raw material powder having said basic composition at the time of calcination step to wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling, molding in a  
20 magnetic field and sintering.

19. The method producing a ferrite magnet according to claim [18] 17, said method comprising the steps of subjecting a raw material powder adjusting to said basic composition at the time of wet-fine pulverizing step to wet-pulverizing to a fine powder having an average diameter ranging  
25 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling,

molding in a magnetic field and sintering.

20. The method producing a ferrite magnet according to claim 18 or 19, wherein 0.2-2.0 weight % of a dispersant per a solid component is added at the time of pulverizing or milling.

5 21. A method for producing a ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rear earth elements including Y, at least one element selected from the group

10 consisting of La, Nd, Pr and Ce being an indispensable element, M is at least two elements selected from the group consisting of Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

15  $[x/(2.6n)] \leq y \leq [x/(1.6n)],$  and

$$5 \leq n \leq 6,$$

said method comprising the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu m$  and said basic composition successively to drying or concentrating, milling, molding in a magnetic  
20 field and sintering.

22. The method producing a ferrite magnet according to claim 21, said method comprising the steps of subjecting a raw material powder having said basic composition at the time of calcination step to wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu m$ , and  
25 thereafter successively to drying or concentrating, milling, molding in a

magnetic field and sintering.

23. The method producing a ferrite magnet according to claim 21, said method comprising the steps of subjecting a raw material powder adjusting to said basic composition at the time of wet-fine pulverizing step to

5 wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling, molding in a magnetic field and sintering.

24. The method producing a ferrite magnet according to claim 22 or 23, wherein 0.2-2.0 weight % of a dispersant per a solid component is added at

10 the time of pulverizing or milling.

## DETAILED DESCRIPTION OF THE INVENTION

[0001]

### Field of the Invention

The present invention relates to a method for producing a  
5 high-performance ferrite magnet having substantially a  
magnetoplumbite-type crystal structure extremely useful for wide ranges of  
magnet applications such as rotors for automobiles or electric apparatuses,  
magnet rolls for photocopiers, etc., particularly to a high-performance  
ferrite magnet having a microstructure having a higher residual magnetic  
10 flux density (Br) or higher residual magnetic flux density (Br) and higher  
coercivity (iHc) than those of the conventional ferrite magnets.

[0002]

### Prior Art

Ferrite magnets are widely used in various applications including  
15 rotors of motors, electric generators, etc. Recently, ferrite magnets having  
higher magnetic properties are required particularly for the purposes of  
miniaturization and reduction in weight in the field of rotors for  
automobiles and increase in performance in the field of rotors for electric  
apparatuses.

20 High-performance sintered magnets such as Sr ferrite or Ba ferrite  
are conventionally produced through the following processes. First, iron  
oxide is mixed with a carbonate of Sr or Ba and then calcined to cause a  
ferritization reaction (ferrite-forming reaction). The resultant calcined  
clinker is coarsely pulverized, mixed with SiO<sub>2</sub>, SrCO<sub>3</sub> and CaCO<sub>3</sub> for  
25 controlling sintering behavior and Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>, etc. for controlling iHc,

and then finely pulverized to an average diameter of 0.7-1.2  $\mu\text{m}$ . A slurry containing the finely pulverized ferrite-forming material is wet-molded while being oriented in a magnetic field to obtain a mold. The resultant mold is sintered and then machined to a desired shape.

5 [0003]

### **Problems to be Solved by the Invention**

To increase the properties of the ferrite magnets produced according to the method mentioned above as a prerequisite, there are the following five methods available.

10 The first method is a fine pulverization method. When the size of crystal grains in the sintered body is close to about 0.9  $\mu\text{m}$ , a critical single magnetic domain diameter of a magnetoplumbite (M)-type Sr ferrite magnet, its  $iH_c$  is maximum. Accordingly, fine pulverization may be carried out to an average diameter of 0.7  $\mu\text{m}$  or less, for instance, taking  
15 into consideration the crystal grain growth at the time of sintering. This method is, however, disadvantageous in that finer pulverization leads to poorer water removal at the time of wet molding, resulting in poorer production efficiency.

The second method is to make the sizes of the crystal grains in the  
20 sintered body as uniform as possible. Ideally, the sizes of the crystal grains are made as uniformly as possible equal to the above critical single magnetic domain diameter (about 0.9  $\mu\text{m}$ ), because crystal grains larger than or smaller than this size have low  $iH_c$ . Specific means for achieving high performance in this method is to improve a particle size distribution of  
25 fine powder. In commercial production as a prerequisite, however, other

pulverization apparatuses than ball mills, attritors, etc. cannot but be used, naturally posing limitations in the level of improvement. Also, an attempt was recently published to produce fine ferrite powder having a uniform particle size by a chemical precipitation method. Such method is,  
 5 however, not suitable for industrial mass production.

The third method is to improve crystal orientation affecting magnetic anisotropy. Specific means in this method is to improve the dispersion of ferrite particles in a slurry of fine powder by adding a surfactant, or to increase the intensity of a magnetic field at the time of  
 10 orientation, etc.

The fourth method is to improve the density of a sintered body. A Sr ferrite sintered body has a theoretical density of 5.15 g/cc. Sr ferrite magnets commercially available at present have densities ranging from 4.9 g/cc to 5.0 g/cc, corresponding to 95-97% of the theoretical density.  
 15 Although improvement in Br is expected by increasing the density of a ferrite magnet, a higher density than the above level needs such density-increasing means as HIP, etc. However, the use of such density-increasing means leads to increase in the production cost of ferrite magnets, depriving the ferrite magnets of advantages as inexpensive  
 20 magnets.

The fifth method is to improve a saturation magnetization  $\sigma_s$  or a crystal magnetic anisotropy constant of a ferrite compound per se, which is a main component of the ferrite magnet. It is likely that the improvement in the saturation magnetization  $\sigma_s$  directly leads to improvement in the  
 25 residual magnetic flux density Br of the ferrite magnet. It is also likely

that the improvement in the crystal magnetic anisotropy constant leads to improvement in the coercivity  $H_c$  of the ferrite magnet. The conventional ferrite compound has an M-type (magnetoplumbite-type) crystal structure. Although research is being carried out on W-type ferrite having a higher  
 5 saturation magnetization than that of the M-type ferrite, the W-type ferrite has not been subjected to mass production because of difficulty in the control of a sintering atmosphere.

Widely used at present among the above methods for improving the properties of ferrite magnets are the first to fourth methods, though it is  
 10 difficult to drastically improve the properties of ferrite having a main phase expressed by  $SrO \cdot nFe_2O_3$  by the first to fourth methods for the reasons described below. The first reason is that the above first to fourth methods include conditions lowering productivity or steps difficult to carry out from the aspect of mass production. The second reason is that further  
 15 improvement in magnetic properties, particularly  $B_r$ , is extremely difficult because they are close to the theoretically highest level.

Accordingly, an object of the present invention is to provide a new ferrite magnet excellent remarkably in magnetic properties and a method for producing thereof based on the above fifth method.

20 [0004]

#### **Means to Solve the Problems**

To achieve the above object, the inventors have found a method to replace part of A and Fe elements in the above ferrite composition with other elements by adding other types of metal compounds to a ferrite  
 25 composition expressed by  $AO \cdot nFe_2O_3$ , wherein A is at least one of Sr and



Ba.

The magnetism of the magnetoplumbite-type ferrite magnet is derived from a magnetic moment of Fe ions, with a magnetic structure of a ferri-magnet in which magnetic moment is arranged partially in antiparallel by Fe ion sites. There are two methods to improve the saturation magnetization in this magnetic structure. The first method is to replace the Fe ions at sites corresponding to the antiparallel-oriented magnetic moment with another element, which has a smaller magnetic moment than Fe ions or is non-magnetic. The second method is to replace the Fe ions at sites corresponding to the parallel-oriented magnetic moment with another element having a larger magnetic moment than Fe ions.

Also, increase in a crystal magnetic anisotropy constant in the above magnetic structure can be achieved by replacing Fe ions with another element having a stronger interaction with the crystal lattice. Specifically, Fe ions are replaced with an element in which a magnetic moment derived from an orbital angular momentum remains or is large.

With the above findings in mind, an enormous research has been conducted in detail for the purpose of replacing Fe ions with various elements by adding various metal oxides. As a result, it has been found that Mn, Co, Ni and Zn are elements remarkably improving magnetic properties. However, the mere addition of the above elements would not provide ferrite magnets with fully improved magnetic properties, because the replacement of Fe ions with other elements would destroy the balance of ion valance, resulting in the generation of undesirable phases. To avoid this phenomenon, ion site of Sr or Ba should be replaced with other

elements for the purpose of charge compensation. Thus, it has been revealed that, for this purpose, the addition of at least one selected from a group consisting of La, Nd, Pr and Ce is effective. The present invention has been completed based upon this

5 [0005]

Thus, the ferrite magnet the present invention has a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rare earth  
10 elements including Y, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

15  $5 \leq n \leq 6,$

and has a substantially magnetoplumbite-type crystal structure.

[0006]

Also, the ferrite magnet the present invention has a basic composition represented by the following general formula:

20  $(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rare earth elements including Y, at least one element selected from the group consisting of Nd, Pr and Ce being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and

25 x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

and has a substantially magnetoplumbite-type crystal structure.

5 [0007]

Further, the ferrite magnet the present invention has a basic composition represented by the following general formula:

$$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3] \text{ by atomic ratio,}$$

wherein A is at least one of Sr and Ba, R is at least one of rare earth

10 elements including Y, at least one element selected from the group consisting of La, Nd, Pr and Ce being an indispensable element, M is at least two elements selected from the group consisting of Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

15  $0.01 \leq x \leq 0.4,$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

and has a substantially magnetoplumbite-type crystal structure.

[0008]

20 The above ferrite magnet of the present invention further comprises preferably 0.05-0.5 weight % of SiO<sub>2</sub> and 0.35-0.85 weight % of CaO per the basic composition, thereby having a higher Br or higher Br and iHc than those of the conventional ferrite magnets.

Also, the ferrite magnet of the present invention formed by  
25 adjusting its composition to the basic composition at the time of calcination

step often shows that the distribution of the R element and/or the M element are much more in crystal grain boundaries than in the magnetoplumbite-type crystal grains. Further, the ferrite magnet of the present invention formed by adjusting its composition to the basic composition at the time of fine pulverization step often shows that the distribution of said R element and/or said M element are much more in crystal grain boundaries than in the magnetoplumbite-type crystal grains.

[0009]

Further, the ferrite magnet the present invention is a method for producing a ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rare earth elements including Y, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

and the method comprises the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu\text{m}$  and the basic composition successively to drying or concentrating, milling, molding in a magnetic field and sintering.

[0010]

Still further, the ferrite magnet the present invention is a method for

producing a ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rear earth

5 elements including Y, at least one element selected from the group consisting of Nd, Pr and Ce being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

10  $[x/(2.6n)] \leq y \leq [x/(1.6n)],$  and

$$5 \leq n \leq 6,$$

and the method comprises the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu m$  and the basic composition successively to drying or concentrating, milling, molding in a magnetic  
15 field and sintering.

[0011]

Still further, the ferrite magnet the present invention is a method for producing a ferrite magnet having a basic composition represented by the following general formula:

20  $(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rear earth

elements including Y, at least one element selected from the group

consisting of La, Nd, Pr and Ce being an indispensable element, M is at

least two elements selected from the group consisting of Mn, Co, Ni and Zn,

25 Co being an indispensable element, and x, y and n are numbers meeting the

following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

- 5 and the method comprises the steps of subjecting a raw material powder having an average diameter of 0.4-0.9  $\mu\text{m}$  and the basic composition successively to drying or concentrating, milling, molding in a magnetic field and sintering.

[0012]

- 10 The high-performance ferrite magnet of the present invention can be produced by subjecting a raw material powder adjusted the basic composition at the time of calcination step in the above method for producing the ferrite magnet to wet-pulverizing to a fine powder having an average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying  
15 or concentrating, milling, molding in a magnetic field and sintering.

- Also, the high-performance ferrite magnet of the present invention can be produced by subjecting a raw material powder adjusted the basic composition at the time of fine pulverization step in the above method for producing the ferrite magnet to wet-pulverizing to a fine powder having an  
20 average diameter ranging 0.4-0.9  $\mu\text{m}$ , and thereafter successively to drying or concentrating, milling, molding in a magnetic field and sintering.

- Further, it is preferable to add 0.2-2.0 weight % of a dispersant per a solid component at the time of pulverizing step or milling step, thereby providing a higher Br or higher Br and iHc than those of the conventional  
25 ferrite magnets.

[0013]

In the ferrite magnet of the present invention, the percentage of La in R is preferably 50 atomic % or more, more preferably 70 atomic % or more, particularly preferably 99 atomic % or more to improve saturation magnetization thereof. To improve the saturation magnetization ( $\sigma_s$ ), the case of R = La except inevitable impurities is ideal.

Also, in the ferrite magnet of the present invention, the total percentage of one or more of Nd, Pr and Ce in R is preferably 50 atomic % or more, more preferably 70 atomic % or more, particularly preferably 99 atomic % or more, and to improve saturation magnetization thereof, R ideally comprises only one or more of Nd, Pr, and Ce except inevitable impurities.

Further, in the ferrite magnet of the present invention, the total percentage of one or more of La, Nd, Pr and Ce in R is preferably 50 atomic % or more, more preferably 70 atomic % or more, particularly preferably 99 atomic % or more, and to improve saturation magnetization thereof, R ideally comprises only one or more of La, Nd, Pr, and Ce except inevitable impurities.

Accordingly, as the R element supplying raw material, inexpensive Misch metals (mixed rare earth elements) containing 50 atomic % or more of one or more of La, Nd, Pr and Ce may also be favorably used.

As the M element, although the ferrite magnet of the present invention may be composed of any of Mn, Co, Ni and Zn, Co is particularly preferable to obtain higher  $iH_c$ . As the magnetic properties, when  $iH_c$  is regarded as more important, the percentage of Co in the M

elements is preferably 50 atomic % or more, more preferably 70 atomic % or more. Also, when Br is regarded as more important, the percentage of Zn or Mn, Ni in the M elements is preferably increased, but, even in this case, the percentage of Co in the M element is preferably 10 atomic % or  
5 more, more preferably 10 atomic % or more to less than 50 atomic %, particularly preferably 10 atomic % or more to less than 30 atomic %.

To impart good magnetic properties to the ferrite magnet of the present invention, the value of n (molar ratio) should be between 5 and 6. When the value of n exceeds 6, undesirable phases such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> other  
10 than the magnetoplumbite phase are generated, resulting in drastic decrease in magnetic properties. On the other hand, when the value of n is less than 5, Br of the ferrite magnet drastically decreases.

The value of x is between 0.05 and 0.4. When the value of x is less than 0.05, sufficient effects related to the present invention cannot be  
15 obtained. On the other hand, when the value of x exceeds 0.4, the magnetic properties of the ferrite magnet conversely rather decrease.

With respect to the relations between the value of x and that of y, to attain the object of the charge compensation, it is necessary to satisfy the relation of  $y = x/(2.0n)$ . When the value of y is between  $x/(1.6n)$  and  
20  $x/(2.6n)$ , the effects of the present invention are not substantially impaired. When value of y deviates from  $x/(2.0n)$ , there is likelihood that Fe<sup>2+</sup> is contained, though there are no problems. Further, when the value of y is deviated from the above range, or even when the contents of the R element and the M element meet the equation of  $y = x/(2.0n)$ , part of the R element  
25 and/or the M element may be maldistributed in the vicinity of grain



boundaries, without causing any problems.

[0014]

In the standard process for producing ferrite magnets essentially comprising the steps of

5            mixing of starting material powders → calcination → fine  
             pulverization of calcined powder → molding → sintering,  
the above basic composition of the ferrite magnet may be substantially achieved at the calcination step.

That is, the R element and the M element are to undergo two time  
10   heating at a high temperature at the time of calcination and sintering by  
adding at the time of mixing in the above steps, whereby the solid diffusion proceeds to provide a uniform composition. However, it is not substantially destroy the effects of the present invention to obtain substantially the same ferrite magnet composition of the present invention  
15   by adding oxides of the R element and oxides of the M element at the time of the pulverization step in the above standard process for producing.

To obtain the high-performance ferrite sintered body, it is preferable to add  $\text{SiO}_2$  and  $\text{CaO}$  ( $\text{CaCO}_3$ ) as elements for controlling a sintering phenomenon at the pulverization step.

20             $\text{SiO}_2$  is an additive for suppressing crystal grain growth at the sintering step, and the amount of  $\text{SiO}_2$  added is preferably 0.05-0.5 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %. When the amount of  $\text{SiO}_2$  added is less than 0.05 weight %, excessive crystal grain growth takes place at the sintering step, resulting in  
25   decrease in coercivity. On the other hand, when the amount of  $\text{SiO}_2$  added

exceeds 0.50 weight %, crystal grain growth is excessively suppressed, resulting in insufficient improvement in orientation that occurs simultaneously with the crystal grain growth, which leads to decrease in Br.

On the other hand, CaO is an element for accelerating the crystal grain growth, and the amount of CaO added is preferably 0.35-0.85 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %. When the amount of CaO added exceeds 0.85 weight %, excessive crystal grain growth takes place at the sintering step, resulting in decrease in coercivity. On the other hand, when the amount of CaO added is less than 0.35 weight %, crystal grain growth is excessively suppressed, resulting in insufficient improvement in orientation that occurs simultaneously with the crystal grain growth, which leads to decrease in Br.

[0015]

To obtain the further high-performance ferrite sintered body from the composition mentioned above, it is preferable to produce it by the following method in place of the above standard process. Namely, it is preferable to choose a technical means such that the above basic composition of the ferrite magnet is subjected to pulverizing in a wet state until the average diameter of the powder mixture becomes 0.4-0.9  $\mu\text{m}$ , and thereafter a slurry of finely pulverized powder is concentrated or dried, crumbled, milled, wet-molded and then sintered.

When pulverization is carried out to an average diameter of less than 0.4  $\mu\text{m}$ , undesirable crystal grain growth takes place at the sintering step, resulting in decrease in coercivity and the deterioration of water removal characteristics at the wet-molding step. Also, when the average

diameter of the powder exceeds 0.9  $\mu\text{m}$ , there are a lot of coarse crystal grains in the structure of the ferrite sintered body.

The important requirements for obtaining the high-performance ferrite magnet are that the composition of the ferrite powder used should be properly controlled, and that the ferrite powder should not be agglomerated in a slurry. As a result of investigation to achieve a state in which each particle of the ferrite powder exists independently in the slurry, it has been found that the agglomeration of ferrite powder is destroyed due to application of a shearing force by drying or concentrating a ferrite powder slurry obtained by the wet-fine pulverization of ferrite powder, adding a dispersant to the resultant high-concentration slurry and milling the slurry, resulting in improvement in orientation of ferrite magnet powder, which leads to improvement in magnetic properties. It has also been found that by adding a dispersant to the slurry at a mixing step, good dispersion can be achieved due to surface modification of ferrite magnet powder by the adsorption of the dispersant, resulting in further improvement in a magnetic force of the ferrite magnet.

Known as dispersants are surfactants, higher aliphatic acids, higher aliphatic acid soap, higher aliphatic acid esters, etc. It has been found that the dispersion of ferrite particles can be improved by using a polycarboxylic acid dispersant, one of anionic surfactants, effectively preventing the agglomeration of ferrite particles. There are many types of polycarboxylic acid dispersants, and particularly effective for improvement in the dispersion of ferrite particles among them is an ammonium salt of polycarboxylic acid.

The amount of the dispersant added is preferably 0.2 weight % or more, per a solid component in the fine powder slurry, thereby obtaining effects of adding the dispersant. When the amount of the dispersant added exceeds 2 weight %, the residual magnetic flux density (Br) conversely  
 5 decreases.

Incidentally, the adjustment so as to form the basic composition of the ferrite magnet at the milling step mentioned above may be carried out.  
 [0016]

### **Operative Embodiments for Practicing the Invention**

10 The present invention will be described in detail below referring to EXAMPLES.

[EXAMPLES 1-6 and REFERENCE EXAMPLES 1-7]

SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, oxides of R elements and oxides of M elements were formulated to provide the following basic composition:

15 (Sr<sub>1-x</sub>R<sub>x</sub>)O·n[(Fe<sub>1-y</sub>M<sub>y</sub>)<sub>2</sub>O<sub>3</sub>] by atomic ratio,  
 wherein n = 6.0, x = 2ny, and x = 0.15,  
 wet-mixed, and then calcined at 1200°C for 2 hours in the air. La, Pr, Nd, Ce, Sm, Eu and Gd were selected as the R element under the criterion that these elements had ion radii close to a radius of an Sr ion. Also, Ti, V, Mn,  
 20 Co, Ni, Cu and Zn were selected as the M elements under the criterion that they had ion radii close to a radius of an Fe ion.

As COMPARATIVE EXAMPLE, a ferrite composition in which n = 6.0 and x = y = 0 in the above basic composition was calcined in the same manner.

25 Each calcined powder was coarsely pulverized in a dry state by a

roller mill, and each of the resultant coarse powder was measured with respect to magnetic properties by a vibration-type magnetometer. The highest intensity of a magnetic field in which measurement was carried out was 12 kOe, and a saturation magnetization  $\sigma_s$  and  $H_c$  were determined by  $\sigma-1/H^2$  plot. The resultant phases of the coarse powder were identified by X-ray diffraction, with the results summarized in Table 1. It is appreciated from Table 1 that when Cu was not contained as the M element, only X-ray diffraction peaks for a magnetoplumbite phase (M phase) were observed in any powder. It is also appreciated from Table 1 that when La was selected as the R element, and one or two of Co, Ni or Zn was selected as the M element, respectively, the resultant calcined powder had higher  $\sigma_s$  and  $H_c$  than that in COMPARATIVE EXAMPLE, suggesting that such calcined powder had a potential that a high-performance, bulk ferrite magnet could be formed therefrom by sintering. Particularly, it seems that when Mn + Co, Ni + Co and Zn + Co were selected as the M elements for the combined replacement elements containing Co, the resultant calcined powder would have such a potential that a high-performance, bulk ferrite magnet could be formed therefrom by sintering.

Further, the ferrite magnets of the present invention may be doubtlessly formed under the same conditions as for producing the ferrite magnet in the EXAMPLES mentioned below except for using any one of combinations between (La) and (Mn + Ni), (La) and (Mn + Co + Ni), (La) and (Mn + Co + Zn), (La) and (Co + Ni + Zn), (La) and (Mn + Ni + Zn), and (La) and (Mn + Co + Ni + Zn), respectively. In these cases, the percentage of Co contained in the M elements is preferably 10 atomic % or

more to have higher Br and iHc than those of the conventional ferrite magnets.

As shown in Table 2, when at least one element of Pr, Nd and Ce is selected as the R element and at least one element of Mn, Co, Ni and Zn is  
5 selected as the M element, the ferrite magnets of the present invention can be formed under the same conditions as for producing the ferrite magnet in the EXAMPLES mentioned below except for forming a R plus M composition comprising each combination of the selected R element and the selected M element. In this connection, Table 2 shows that when Pr,  
10 for instance, is selected as the R element, any one of total 15 different combinations of Mn, Co, . . . , (Mn + Co + Ni + Zn) can be selected as the M element. Further, in case of R = (Pr + Nd + Ce), also any one of total 15 different combinations in the same manner as those mentioned above can be selected as the M element.

15

[0017]

Table 1

No.	R Element	M Element (atomic %)	$\sigma_s$ (emu/g)	H <sub>c</sub> (kOe)	Phase Produced
Ref. Ex. 1	La	100Ti	64.6	3.1	M Phase
Ref. Ex. 2		50Ti + 50Co	62.1	0.8	M Phase
Ref. Ex. 3		100V	59.0	6.4	M Phase
Ref. Ex. 4		50V + 50Co	59.1	6.4	M Phase
Ex. 1		100Mn	67.1	3.7	M Phase
Ex. 2		50Mn + 50Co	66.8	3.9	M Phase
Ex. 3		100Co	66.0	4.5	M Phase
Ex. 4		100Ni	66.1	2.9	M Phase
Ex. 5		50Ni + 50Co	65.9	3.5	M Phase
Ref. Ex. 5		100Cu	65.8	0.3	M Phase + Undesirable Phase
Ref. Ex. 6		50Cu + 50Co	65.1	1.2	M Phase + Undesirable Phase
Ref. Ex. 7		100Zn	68.9	3.1	M Phase
Ex. 6		50Zn + 50Co	67.8	3.6	M Phase
Com. Ex.	-	-	65.4	3.1	M Phase

[0018]

Table 2

R Element	M Element
Pr	Mn Co
Nd	Ni Zn
Ce	Mn + Co Mn + Ni
Pr + Nd	Mn + Zn Co + Ni
Pr + Ce	Co + Zn Ni + Zn
Nd + Ce	Mn + Co + Ni Mn + Co + Zn
Pr + Nd + Ce	Mn + Ni + Zn Co + Ni + Zn Mn + Co + Ni + Zn

[0019]

5 [EXAMPLES 7-9 and REFERENCE EXAMPLE 8]

La was selected as the R element, Mn (EXAMPLE 7), Co (EXAMPLE 8), Ni (EXAMPLE 9) and Zn (REFERENCE EXAMPLE 8) were selected as the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and oxides of the M elements were formulated to provide the following basic composition:

10

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.117$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and

15 then finely pulverized in a wet state by an attritor to produce a slurry



containing fine powder of  $0.7\ \mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0.40 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), respectively, based on the weight of the coarse powder. Each of the  
5 resultant fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at  $1180\text{--}1230^\circ\text{C}$  for 2 hours. Also, as COMPARATIVE MATERIAL (CONVENTIONAL FERRITE MAGNET), a ferrite composition in which  $n = 6.0$  and  $x = y = 0$  in the above basic composition was produced in the same manner. Each  
10 of the resultant sintered bodies was machined to a shape of about  $10\ \text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 1.

It is understood from Fig. 1 that residual magnetic flux density  $B_r$  of each of (La, Mn)-, (La, Ni)- and (La, Zn)-containing ferrite magnets  
15 extends favorably in a low  $iH_c$  region as compared with that of the conventional ferrite magnet, its effect on the improvement in saturation magnetization ( $\sigma_s$ ) is remarkably increased. Accordingly, any one of the (La, Mn)-, (La, Ni)- and (La, Zn)-containing ferrite magnets is particularly suitable for the high  $B_r$  materials. Whereas, the (La, Co)-containing  
20 ferrite magnet has both a comparatively favorable value of  $B_r$  and a high value of  $iH_c$ , so that this is utmost promising for the high performance materials. As shown in this EXAMPLE, it is clear that the invented ferrite magnets are advantageous over the conventional ferrite magnet.

Incidentally, also in the sintered body produced in the same manner  
25 in EXAMPLES 7-9 except that  $\text{BaCO}_3$  or ( $\text{SrCO}_3$  and  $\text{BaCO}_3$ ) is used in

place of  $\text{SrCO}_3$  in the mixing step before calcination, that is, in the invented ferrite magnet with Ba or (Sr + Ba) selected as the A element, the higher Br or higher Br and iHc than that of the conventional ferrite magnet may be achieved.

5 [0020]

[EXAMPLE 10]

La was selected as the R element and Co + Zn were doubly added as the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and oxides of the M elements were formulated to provide the following basic composition:

10  $(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio, wherein  $\text{M} = \text{Co}_{1-z}\text{Zn}_z$ , and wherein  $n = 5.85$ ,  $x = 2ny$ ,  $x = 0.15$  and  $z = 0-0.5$ , wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry  
15 containing fine powder of  $0.8\ \mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0.40 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as CaO), respectively, based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10  
20 kOe, and each of the resultant green bodies was sintered at  $1180-1230^\circ\text{C}$  for 2 hours. Each of the resultant sintered bodies was machined to a shape of about  $10\ \text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 2.

It is understood from Fig. 2 that when La is added as the R element  
25 and Co + Zn are add as the M elements, respectively, higher magnetic

properties than those of the conventional magnets can be achieved also, and it is preferable to increase the Co content (preferably,  $Z \leq 0.3$ ) when higher iHc is required, and it is also preferable to increase the Zn content (preferably,  $0.3 < Z \leq 0.9$ ) when higher Br is required.

Incidentally, the ferrite magnets having the Co content of 10 atomic % or more per the total amount of the M elements comprising Co and Zn are extremely useful for various rotors, actuators, etc. required to have high Br and iHc. When the Co content is less than 10 atomic % extremely reduces iHc.

[0021]

[EXAMPLE 11]

Any one of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb, and Co were selected as the R element and the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and oxides of the R element were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.15$ ,

wet-mixed, and then calcined at  $1250^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.8 \mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0.40 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as CaO), respectively, based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10

kOe, and each of the resultant green bodies was sintered at 1180-1230°C for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 3.

5 It is understood from Fig. 3 that any one of La, Ce, Pr and Nd is added as the R element and Co is added as the M elements, respectively, higher magnetic properties than those of the conventional magnets can be achieved.

Further, the ferrite magnets of the present invention should be formed in the same manner in the above EXAMPLE 11 except for using the combined replacement elements, for instance, La + Pr or La + Nd in place of La. Effective combinations of the R element and the M element (Co) are specifically illustrated by examples in Table 3.

[0022]

15

Table 3

R Element	M Element
La + Pr	Co
La + Nd	
La + Ce	
La + Pr + Nd	
La + Pr + Ce	
La + Nd + Ce	
La + Pr + Nd + Ce	

[0023]

[EXAMPLE 12]

Sr, La and Co were selected as the A element, the R element and the M element, respectively, and SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> were

20

formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Co}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 6.0$ ,  $x = 2ny$ , and  $x = 0-0.6$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. Thereafter,

5 the coarse powder was produced by the method in the same manner as in  
EXAMPLE 1, and the magnetic properties of the resultant coarse powder  
were measured. The results are shown in Fig. 4.

It is appreciated from Fig. 4 that the simultaneous addition of  $\text{La}_2\text{O}_3$   
and  $\text{Co}_3\text{O}_4$  remarkably improves  $i\text{Hc}$ . Also,  $\text{Br}$  was substantially constant  
10 or no remarkable decrease in its value. Further, when the value of the  
addition amount  $x$  exceeds 0.05, its effects were remarkable, and when the  
value of  $x$  exceeds 0.5, its effects decreased. Thus, the value of  $x$  is  
preferably between 0.01 and 0.5, more preferably between 0.07 and 0.4.  
Further, it has been confirmed that when the value of  $n$  was between 5.0  
15 and 6.0, there was no significant difference, thereby obtaining the same  
effects as mentioned above.

Further, as a result of evaluating the saturation magnetization ( $\sigma_s$ )  
and  $\text{Hc}$  with respect to  $x$  in the same manner in EXAMPLE 12 mentioned  
above except for using a combination of any one of the R elements with  
20 any one of the M elements shown in Table 4 (for instance, when the R  
elements were  $\text{La} + \text{Pr}$  in place of  $\text{La}$ , and the M elements were  $\text{Co} + \text{Zn}$ ,  
etc.), the results indicated substantially the same tendency as shown in Fig.  
1. Incidentally, the percentage of  $\text{Co}$  in the M elements is 10 atomic % or  
more in all cases.

[0024]

Table 4

R Elements	M Elements
La + Pr	Co + Zn
La + Nd	Co + Mn
La + Ce	Co + Ni
La + Pr + Nd	Co + Mn + Zn
La + Pr + Ce	Co + Mn + Ni
La + Nd + Ce	Co + Zn + Ni
Pr + Nd + Ce	Co + Zn + Mn + Ni
La + Pr + Nd + Ce	

[0025]

## 5 [EXAMPLE 13]

La and Co were selected as the R element and the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

10 wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0-0.5$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.8\ \mu\text{m}$  in average diameter. Added as sintering  
 15 aids at an early stage of the fine pulverization of the coarse powder were 0.40 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at  $1180-1230^\circ\text{C}$  for 2 hours.

Each of the resultant sintered bodies was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 5.

It is understood from Fig. 5 that good magnetic properties can be achieved when the value of x is between 0-0.4, and when x exceeds 0.4, the magnetic properties decrease conversely.

[0026]

[EXAMPLE 14]

To investigate the permissible range of a ratio of the R element to the M element added in connection with charge compensation, Sr, La and Co were selected as the A element, the R element and the M element, respectively, and SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> were formulated in such proportions as to provide the following basic composition:

(Sr<sub>1-x</sub>La<sub>x</sub>)O·n[(Fe<sub>1-y</sub>Co<sub>y</sub>)<sub>2</sub>O<sub>3</sub>] by atomic ratio,

wherein n = 6.0, y = 0.77-2.08 × 10<sup>-2</sup>, and x = 0.15,

wet-mixed, and then calcined at 1200°C for 2 hours. Thereafter, the coarse powder was produced by the method in the same manner as in the above EXAMPLE, and the magnetic properties of the resultant coarse powder were measured.

As a result, it has thus been found that there is no substantial deterioration in magnetic properties, thereby maintaining the effects of the present invention, as long as the ratio of x/ny is within the range of 1.6-2.6, not limited to the conditions under which the charge balance is fully kept, namely to a ratio of x to y satisfying the relation of x = 2ny. On the other hand, when the ratio of x/ny exceeds 2.6 or is less than 1.6, remarkable

decrease in magnetic properties is appreciated. Further, as a result of forming the ferrite magnets in the same manner in the above EXAMPLE except for using the above coarsely pulverized powder, it is appreciated the effect such that when the ratio of  $x/ny$  is within the range of 2-2.6, the  
 5 rectangular characteristic of the B-H curve has been remarkably improved. Accordingly, the ratio of  $x/ny$  should be preferably between 1.6 and 2.6. This condition may be converted to the formula of  $y$  showing a preferable range of the value of  $y$  as follows:

$$[x/(2.6n)] \leq y \leq [x/(1.6n)].$$

10 [0027]

[EXAMPLE 15]

Sr, Nd and Zn were selected as the A element, the R element and the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{ZnO}$  were formulated to provide the following basic composition:

15  $(\text{Sr}_{1-x}\text{Nd}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Zn}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.117$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry

20 containing fine powder of  $0.7 \mu\text{m}$  in average diameter. To investigate the effects of sintering aids on the magnetic properties, added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0-0.60 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight of the coarse powder. Each of the resultant fine  
 25 powder slurries was wet-molded in a magnetic field of 10 kOe, and each of



the resultant green bodies was sintered at 1180-1230°C for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 6. Incidentally, when SiO<sub>2</sub> was 0 weight %, the value of iHc was extremely too low to plot it.

It is clear from Fig. 6 that as the amount of SiO<sub>2</sub> added increases, the iHc increases, and when the amount of SiO<sub>2</sub> added is 0.45 weight %, an appropriate value of iHc is obtained. On the other hand, when the amount of SiO<sub>2</sub> added increases to 0.60 weight %, the dependency of iHc on the sintering temperature becomes unstable. This seems because the effect of SiO<sub>2</sub> to suppress the crystal grain growth is excessively suppressed so that proper grain growth does not take place at the sintering step. Accordingly, it is desirable that the amount of SiO<sub>2</sub> added is preferably between 0.40 and 0.50 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

The above results were obtained in the case of  $n = 5.85$ . However, since the range of the desirable amount of SiO<sub>2</sub> added depends on the value of  $n$ , similar investigations have been carried out when the value of  $n$  is 5.95. In this case ( $n = 5.95$ ), it has been found that the amount of SiO<sub>2</sub> added is preferably between 0.05 and 0.50 weight %.

The dependency of magnetic properties on the amount of CaO added has been investigated, when the amount of SiO<sub>2</sub> added is fixed to be 0.45 weight %. The results are substantially same as those mentioned above. As a result, it has been found that the desirable amount of CaO added is preferably between 0.35 and 0.85 weight %, assuming that the

basic composition of the ferrite magnet is 100 weight %.

Next, as the results of investigation in connection with the influence of the amount of the combined addition of  $\text{SiO}_2$  and  $\text{CaO}$  on the magnetic properties of the sintered body produced by the method in the same manner as in the above EXAMPLE 15 except that La was selected in place of Nd as the R element and Co was selected in place of Zn as the M element, it has been found that the amount of  $\text{SiO}_2$  added is between 0.05 and 0.50 weight % and the amount of  $\text{CaO}$  added is between 0.35 and 0.85 weight, assuming that the basic composition of the ferrite magnet is 100 weight %.

[0028]

[EXAMPLE 16]

La and Co were selected as the R element and the M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.15$ ,

wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry

containing fine powder of  $0.73\ \mu\text{m}$  in average diameter. Also, a slurry containing fine powder of  $0.43\ \mu\text{m}$  in average diameter was produced using a sand mill. On this occasion, added as sintering aids at an early stage of the fine pulverization of the coarse powder were 0.45 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight of the coarse powder. The resultant fine powder slurries containing the fine

powder of 0.73  $\mu\text{m}$  was wet-molded without alternation in a magnetic field of 10 kOe to obtain a green body. On the other hand, the resultant fine powder slurries containing the fine powder of 0.43  $\mu\text{m}$  was dried, and then subjected to milling treatment. The milling was carried out by using a  
5 kneader so that the concentration of a solid component became 85 weight % by adding water therein. On this occasion, to improve the dispersibility, a salt of polycarboxylic acid was added in the amount of 0.4 weight % per a solid component in the fine powder slurry. Thereafter, the sintered body was produced in the same manner as in the case of the fine  
10 powder of 0.73  $\mu\text{m}$ . Each of the resultant green bodies was sintered at 1180-1230°C for 2 hours to produce a sintered body. Also, a sample having a composition of  $x = y = 0$  in the above basic composition was produced in the same manner as a COMPARATIVE MATERIAL (CONVENTIONAL POWDER). Each of the resultant sintered bodies  
15 was machined to a shape of about 10 mm  $\times$  10 mm  $\times$  20 mm to measure magnetic properties by a B-H tracer. The results are shown in Fig. 7.

It is clear from Fig. 7 that both in 0.73  $\mu\text{m}$  and in 0.43  $\mu\text{m}$ , the magnetic properties of the substituted material by La and Co (La, Co-Containing Powder) are advantageous over the conventional powder.  
20 Particularly, the improvement in  $iH_c$  is excellent. Further, the material fine pulverized to a 0.43  $\mu\text{m}$  level and subjected to milling treatment shows improvement in Br by about 150G, thereby revealing the validity of the method according to the present invention.

As the results of further detailed investigation on the influence of the  
25 average diameter of a finely pulverized powder on the magnetic properties,

it has been revealed that the average diameter exceeding 0.9  $\mu\text{m}$  leads to remarkably decrease in the validity of the above method, while the average diameter of less than 0.40  $\mu\text{m}$  results in conversely decrease in the magnetic properties because excessive crystal grain growth takes place at the sintering step. Accordingly, the average diameter of a fine powder after fine pulverization is preferably between 0.40 and 0.90  $\mu\text{m}$ .

Also, as the results of further detailed investigation on the influence of the amount of a dispersant added at the time of milling step on the magnetic properties, it has been revealed that the amount of the dispersant of 0.2 weight % per a solid component does not provide remarkably the effectiveness, and the amount of the dispersant exceeding 2.0 weight % per a solid component results in conversely deterioration in magnetic properties due to the decomposition of organic substances at the time of sintering step. Accordingly, the amount of a dispersant added is preferably between 0.20 and 2.0 weight %.

[0029]

[EXAMPLE 17]

$\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  were formulated to provide a basic composition of  $\text{SrO} \cdot n\text{Fe}_2\text{O}_3$ , wherein  $n = 5.95$ , wet-mixed, and then calcined at 1200°C for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of 0.80  $\mu\text{m}$  in average diameter. At an early stage of the fine pulverization of each coarse powder, 0-5.0 weight % of  $\text{La}_2\text{O}_3$  and 0-2.3 weight % of  $\text{CoO}$ , based on the weight of the coarse powder, were added.

Also, 1.3 weight % of  $\text{Cr}_2\text{O}_3$  was added at an early stage of the fine pulverization of coarse powder to produce a slurry as a comparative material. In any cases, 0.50 weight % of  $\text{SrCO}_3$ , 0.30 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight  
 5 of the coarse powder, were added as sintering aids. The final basic composition obtained when 2.50 weight % of  $\text{La}_2\text{O}_3$  and 1.15 weight % of  $\text{CoO}$  were added approximately corresponds to the following formula:



wherein  $x = 0.15$ ,  $x = 2ny$ , and  $n = 5.85$ .

10 Each of the resultant fine powder slurries containing fine powders of an average diameter of  $0.80 \mu\text{m}$  was wet-molded without alternation in a magnetic field of 10 kOe to obtain a green body. Each of the resultant green bodies was sintered at  $1180\text{-}1230^\circ\text{C}$  for 2 hours to obtain a sintered body. The resultant sintered body was machined to a shape of about 10  
 15  $\text{mm} \times 10 \text{ mm} \times 20 \text{ mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 8.

It is clear from Fig. 8 that the addition of 2.50 weight % of  $\text{La}_2\text{O}_3$  and 1.15 weight % of  $\text{CoO}$  (indicated by “ $\nabla$ ”) greatly improves  $i\text{Hc}$  as compared with no addition (indicated by “ $\circ$ ”), with extremely smaller  
 20 decrease in  $\text{Br}$  in a high  $i\text{Hc}$  region than in the case of the addition of  $\text{Cr}_2\text{O}_3$  that is usually added to increase  $i\text{Hc}$  (indicated by “ $\times$ ”). Further, the useful magnetic property ( $i\text{Hc}$ ) could not be obtained when only  $\text{CoO}$  was added (indicated by “ $\triangle$ ,  $\square$ ”), or when the balance of charge compensation was destroyed (indicated by “ $\diamond$ ”).

This EXAMPLE has not only clarified the effectiveness of the present invention in the case of  $R = \text{La}$  and  $M = \text{Co}$ , but also proved that the effectiveness obtained by adding the R element and the M element at the time of fine pulverization to provide approximately the desired basic composition is substantially same as that obtained by adding the R element and the M element at the time of calcination to provide the desired basic composition.

[0030]

[EXAMPLE 18]

Observation by a transmission electron microscope (TEM) was carried out on thin films formed from samples cut away in an appropriate size from the ferrite magnet ( $x = 0.20$ ) in EXAMPLE 13 of the present invention prepared by adding  $\text{La}_2\text{O}_3$  and  $\text{CoO}$  at a mixing step before calcination. Fig. 9 shows an example of the photograph of a visual field of an arbitrary portion of this sample film observed by TEM, and Fig. 10 shows a schematic diagram corresponding to Fig. 9. Also, Table 5 shows the results of TEM analysis of the point A (within magnetoplumbite-type ferrite crystal grains) and of the point B (in crystal grain boundaries) shown in Fig. 10. Further, Table 6 shows the results of TEM analysis carried out in the same manner except for changing the points to be analyzed.

It is appreciated such tendency from Table 5 that although La (R element) is fully dissolved in the magnetoplumbite-type ferrite crystal grains, it also maldistributed in crystal grain boundaries in larger amounts. In this TEM analysis, the measurements problems make it difficult to detect Co, but the results of SEM (scanning-type electron microscope) analysis

carried out in parallel with TEM analysis have revealed such tendency that Co (M element) is also fully dissolved in the magnetoplumbite-type ferrite crystal grains, while it is also maldistributed in crystal grain boundaries in larger amounts. However, from the results of the analysis (Table 6)

5 performed on other positions in this sample film, it is appreciated such a case that although La (R element) is fully dissolved in the magnetoplumbite-type ferrite crystal grains, they exist in the crystal grains in larger amount. Further, analysis by SEM, etc. at 20 sites in each of the crystal grain boundaries and the crystal grains of this sample film has  
10 revealed that the cases, where La (R element) and/or Co (M element) tend to be higher in concentration in the crystal grain boundaries than in the magnetoplumbite-type ferrite crystal grains, exceed half the total number of the analysis. This clearly has a close relation to the fact that the sample of the ferrite magnet of the present invention was prepared by adding  $\text{La}_2\text{O}_3$   
15 and CoO at the mixing step before calcination.

[0031]

Table 5 (weight %)

Position	Si	Ca	Fe	Sr	La
Position A in Crystal Grain	2.2	-	86.5	8.4	2.9
Position B in Crystal Grain Boundary	17.5	14.0	28.9	33.4	6.2

[0032]

Table 6 (weight %)

Position	Si	Ca	Fe	Sr	La
Position X <sup>1)</sup> in Crystal Grain	2.1	-	86.6	8.2	3.1
Position Y <sup>2)</sup> in Crystal Grain Boundary	15.4	13.6	29.2	41.5	0.3

1): Position different from Position A.

2): Position different from Position B.

5

[0033]

[EXAMPLE 19]

Further, observation by a scanning-type electron microscope (SEM) was carried out on samples cut away in an appropriate size from the ferrite magnet in EXAMPLE 17 of the present invention prepared by adding

10 La<sub>2</sub>O<sub>3</sub> and CoO at a fine pulverization step. Table 7 shows the results of SEM analysis on an arbitrary portion in magnetoplumbite-type ferrite crystal grains and on arbitrary two positions in crystal grain boundaries in these samples.

15 It is clear from Table 7 that La (R element) and Co (M element) are fully dissolved in the magnetoplumbite-type ferrite crystal grains, though they also exist in crystal grain boundaries in large amounts. Further, analysis by SEM, etc. at 20 sites in each of the crystal grain boundaries and the crystal grains of this sample have revealed that La (R element) and/or

20 Co (M element) tend to be higher in concentration in the crystal grain boundaries than in the magnetoplumbite-type ferrite crystal grains. This clearly has a close relation to the fact that the ferrite magnet was prepared



by adding  $\text{La}_2\text{O}_3$  and  $\text{CoO}$  at the fine pulverization step after calcination.

[0034]

Table 7 (weight %)

Position	Si	Ca	Fe	Sr	La	Co
Position (1) in Crystal Grain	1.9	-	85.9	8.3	2.8	1.1
Position (2) in Crystal Grain	2.2	-	85.5	8.3	2.7	1.3
Position (1) in Crystal Grain Boundary	15.7	12.5	25.9	29.9	15.8	0.2
Position (2) in Crystal Grain Boundary	16.6	13.3	27.4	31.5	0.4	10.8

5 [0035]

Although EXAMPLES 18 and 19 indicate a case where  $R = \text{La}$  and  $M = \text{Co}$ , it should be noted that ferrite magnets formed from combinations of other R elements and other M elements in the above EXAMPLES would also have high coercivity  $iH_c$  (or high coercivity  $iH_c$  and residual magnetic flux density  $B_r$ ), as long as they have the same microstructures as in these EXAMPLES.

10

[0036]

Although the above EXAMPLES are related to Sr ferrite replaced with the R element and the M element, it should be noted that also in Ba ferrite or (Sr, Ba) ferrite replaced with the R element and the M element it is possible to obtain a ferrite magnet having substantially a magnetoplumbite-type crystal structure with a higher  $B_r$  or higher  $B_r$  and  $iH_c$  than those of the conventional ferrite magnets.

15

Compounds effective for improving magnetic properties such as

B<sub>2</sub>O<sub>3</sub>, Bi compounds, etc., other than SiO<sub>2</sub> and CaO, or inevitable impurities, may be added to the ferrite magnet of the present invention having a magnetoplumbite-type crystal structure.

[0037]

## 5    **Effects of the Invention**

As mentioned above, the present invention provides a ferrite magnet having substantially a magnetoplumbite-type crystal structure and also showing higher saturation magnetization (Br) or higher saturation magnetization (Br) and coercivity than those of conventional ferrite magnet,  
10    thereby greatly contributing to the development in the wide ranges of magnet applications as a new ferrite magnet excellent in cost performance.

## **Brief Description of the Drawings**

- [Fig. 1]        Fig. 1 is a graph showing an example of the magnetic  
15    properties of the ferrite magnet of the present invention.
- [Fig. 2]        Fig. 2 is a graph showing another example of the magnetic  
properties of the ferrite magnet of the present invention.
- [Fig. 3]        Fig. 3 is a graph showing a further example of magnetic  
properties of the ferrite magnet of the present invention.
- 20    [Fig. 4]        Fig. 4 is a graph showing the correlation between x and  $\sigma_s$ ,  
Hc in the ferrite magnet of the present invention.
- [Fig. 5]        Fig. 5 is a graph showing a still further example of magnetic  
properties of the ferrite magnet of the present invention.
- [Fig. 6]        Fig. 6 is a graph showing the correlation between the  
25    amount of SiO<sub>2</sub>, CaO added and magnetic properties in the ferrite magnet

of the present invention.

[Fig. 7] Fig. 7 is a graph showing the effectiveness of a method according to the present invention.

[Fig. 8] Fig. 8 is a graph showing a still further example of magnetic  
5 properties of the ferrite magnet of the present invention.

[Fig. 9] Fig. 9 is an example of photographs of the structure of the sintered body of the present invention taken by a transmission electric microscope.

[Fig. 10] Fig. 10 is a schematic diagram corresponding to Fig. 9.

10

## ABSTRACT

### Problems to be solved:

To provide a ferrite magnet having substantially a  
5 magnetoplumbite-type crystal structure with higher saturation  
magnetization (Br) or higher saturation magnetization (Br) and coercivity  
(iHc) than those of conventional ferrite magnets and a method for  
producing thereof.

### Solution:

10 A ferrite magnet having a basic composition represented by the  
following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one of rare earth  
elements including Y, La being an indispensable element, M is at least one  
15 element selected from the group consisting of Co, Mn and Ni, and x, y and  
n are numbers meeting the following conditions:

$$0.01 \leq x \leq 0.4,$$

$$[x/(2.6n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5 \leq n \leq 6,$$

20 the ferrite magnet substantially having a magnetoplumbite-type crystal  
structure.

**Selected Drawings:** Fig. 1

FIG. 1

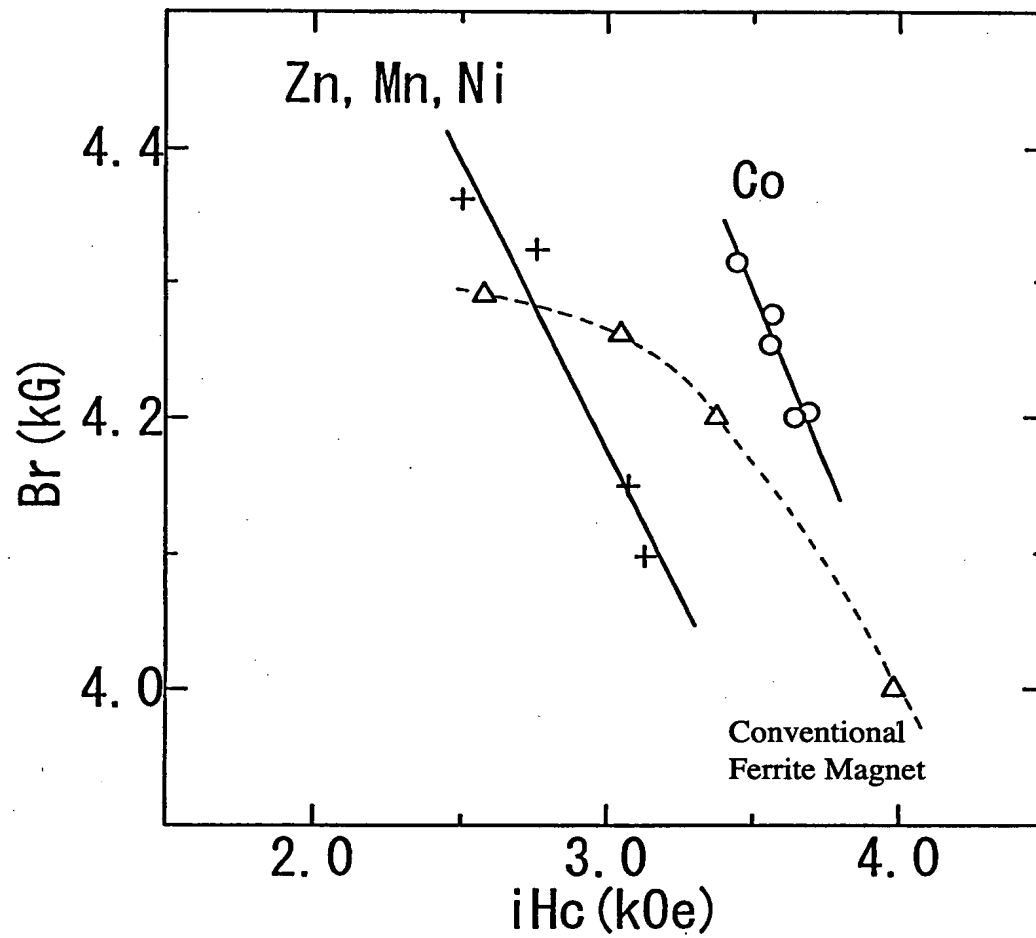


FIG. 2

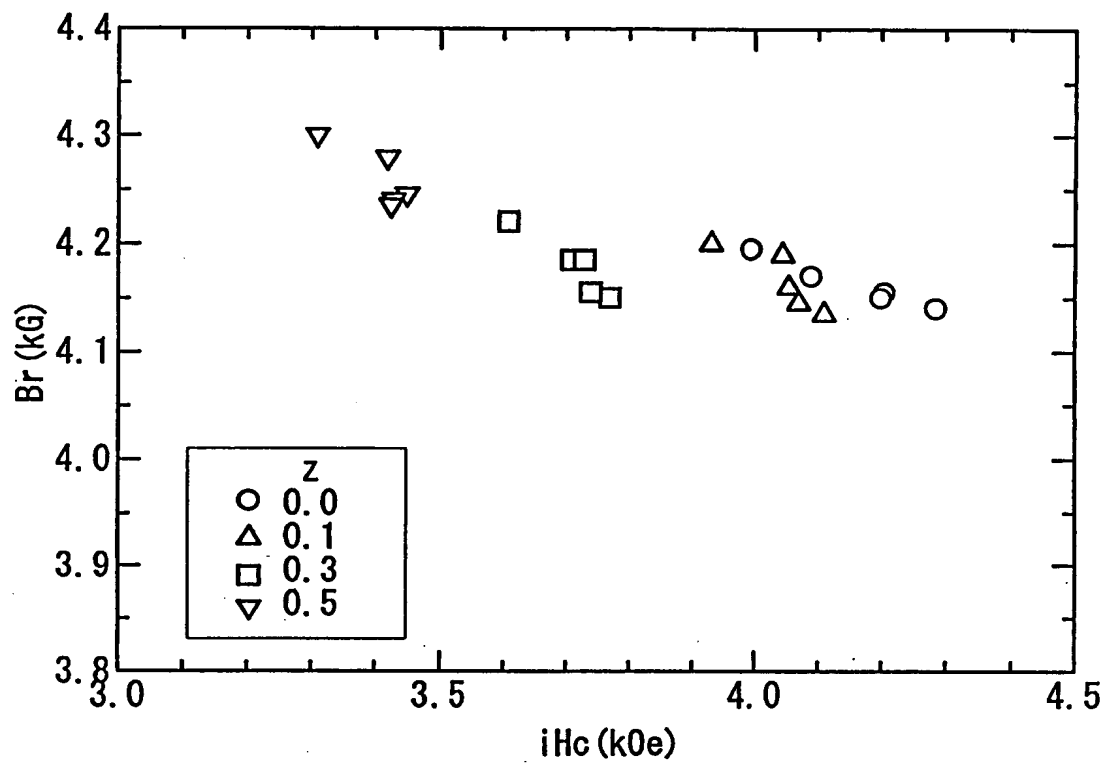


FIG. 3

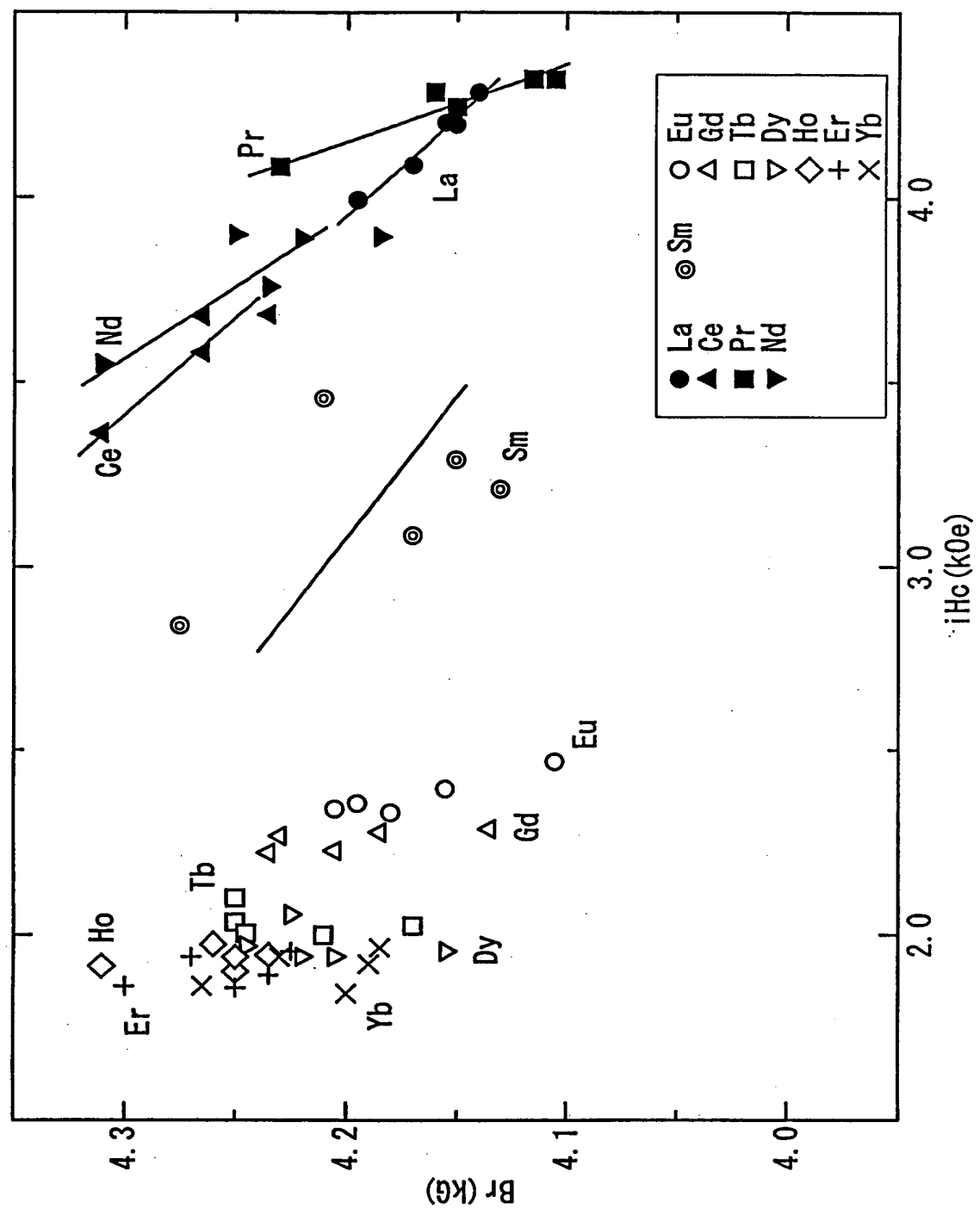


FIG. 4

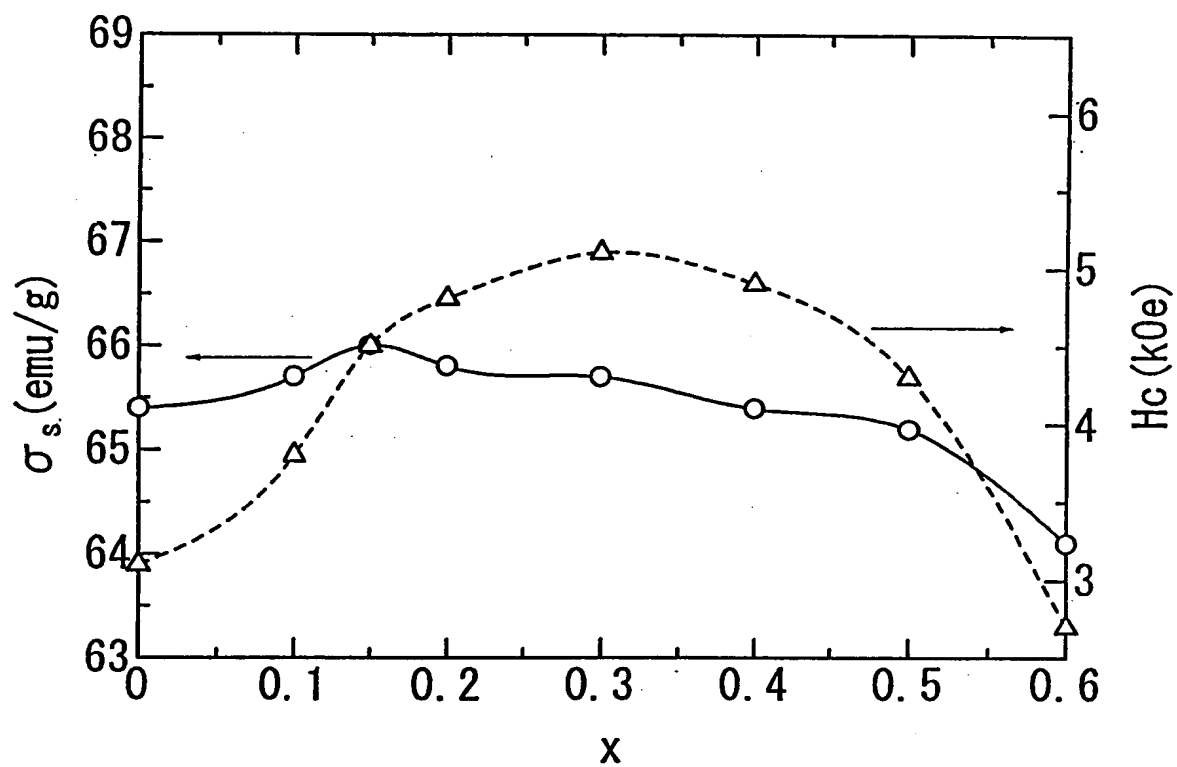




FIG. 5

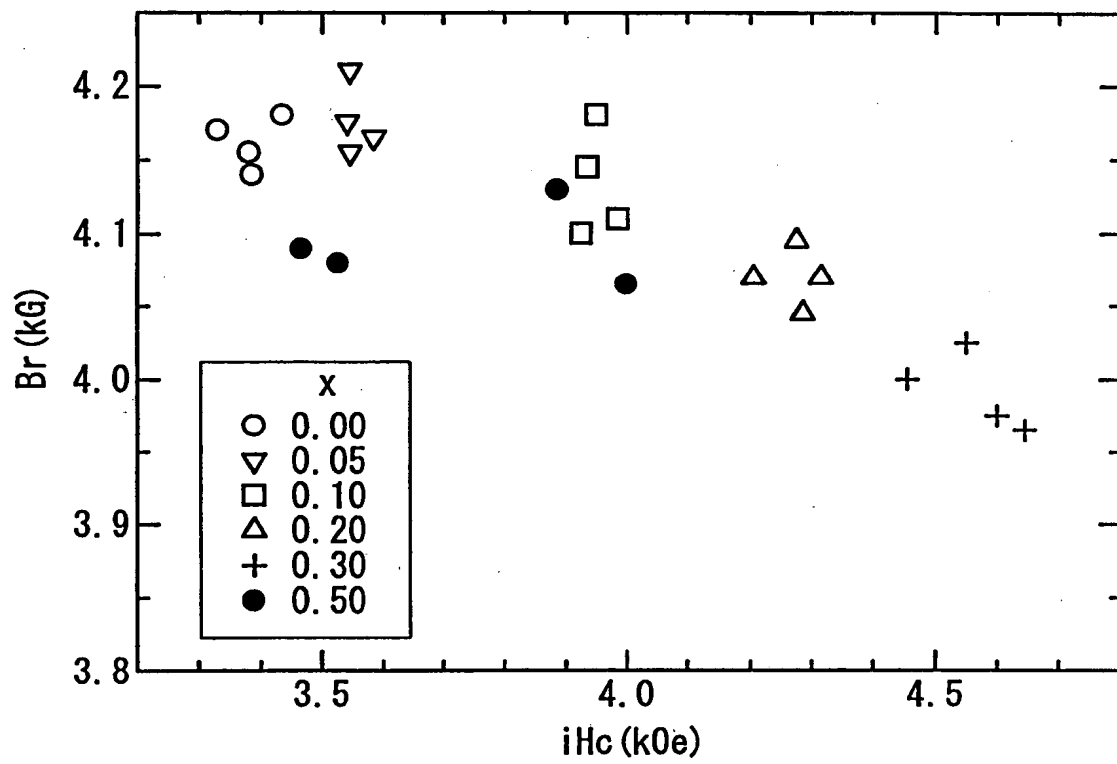


FIG. 6

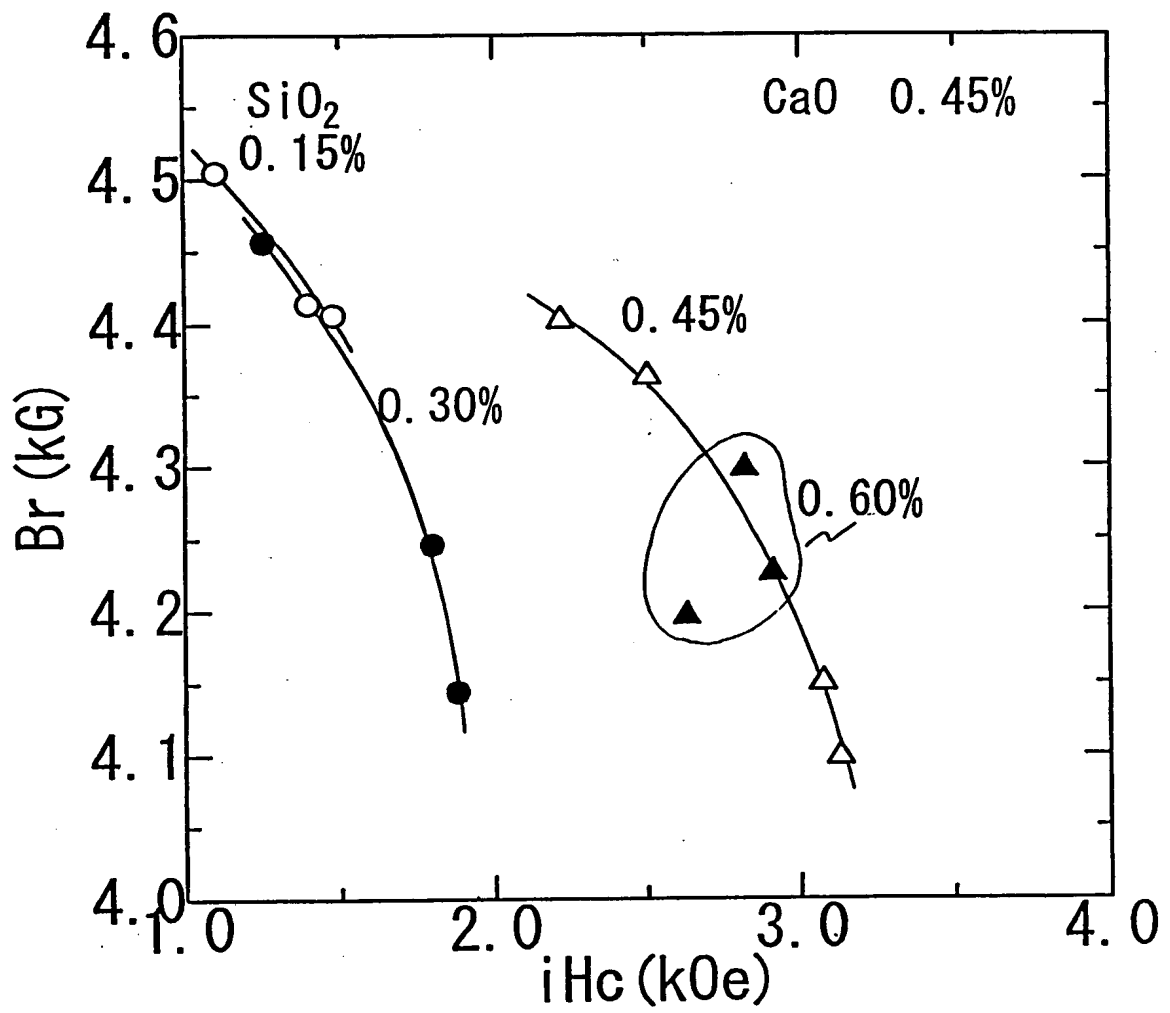


FIG. 7

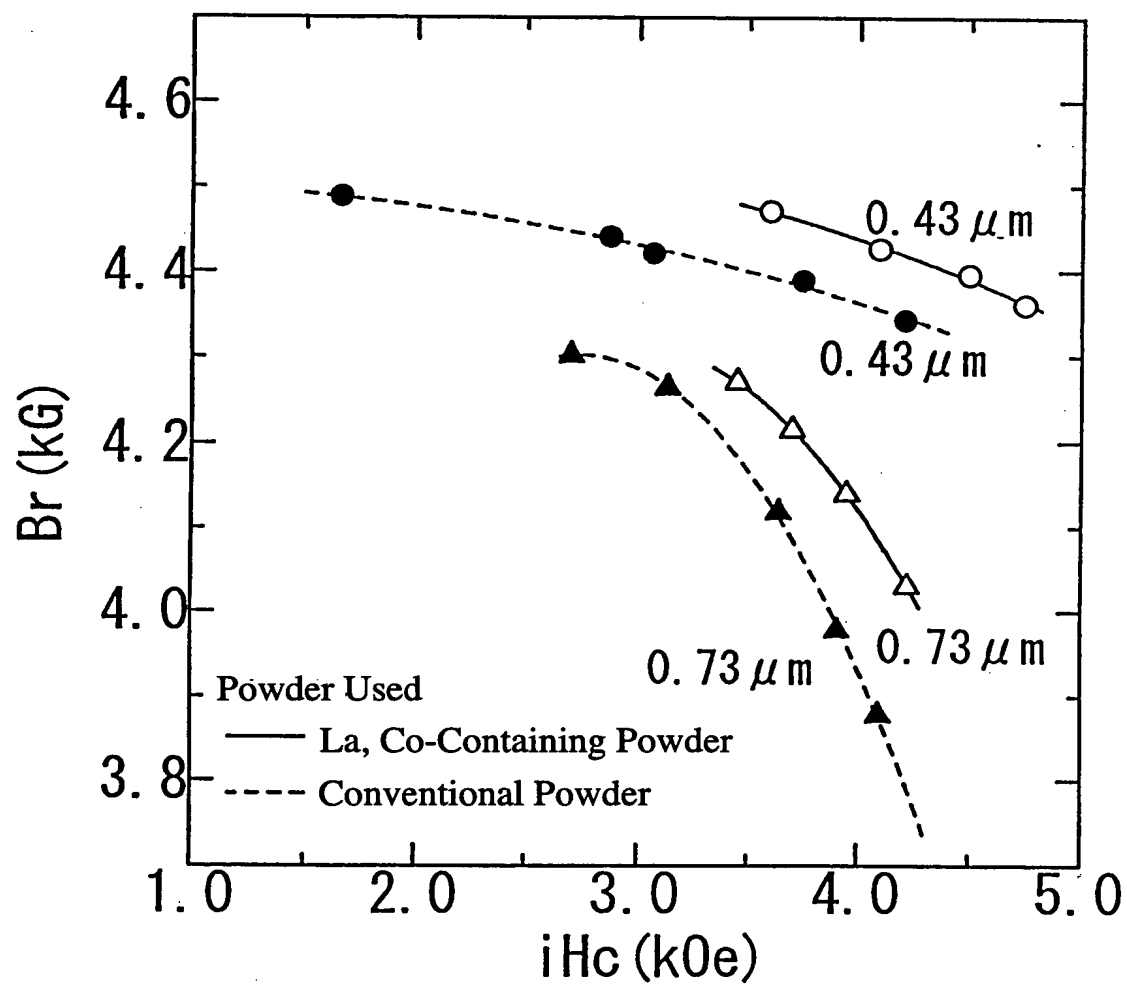


FIG. 8

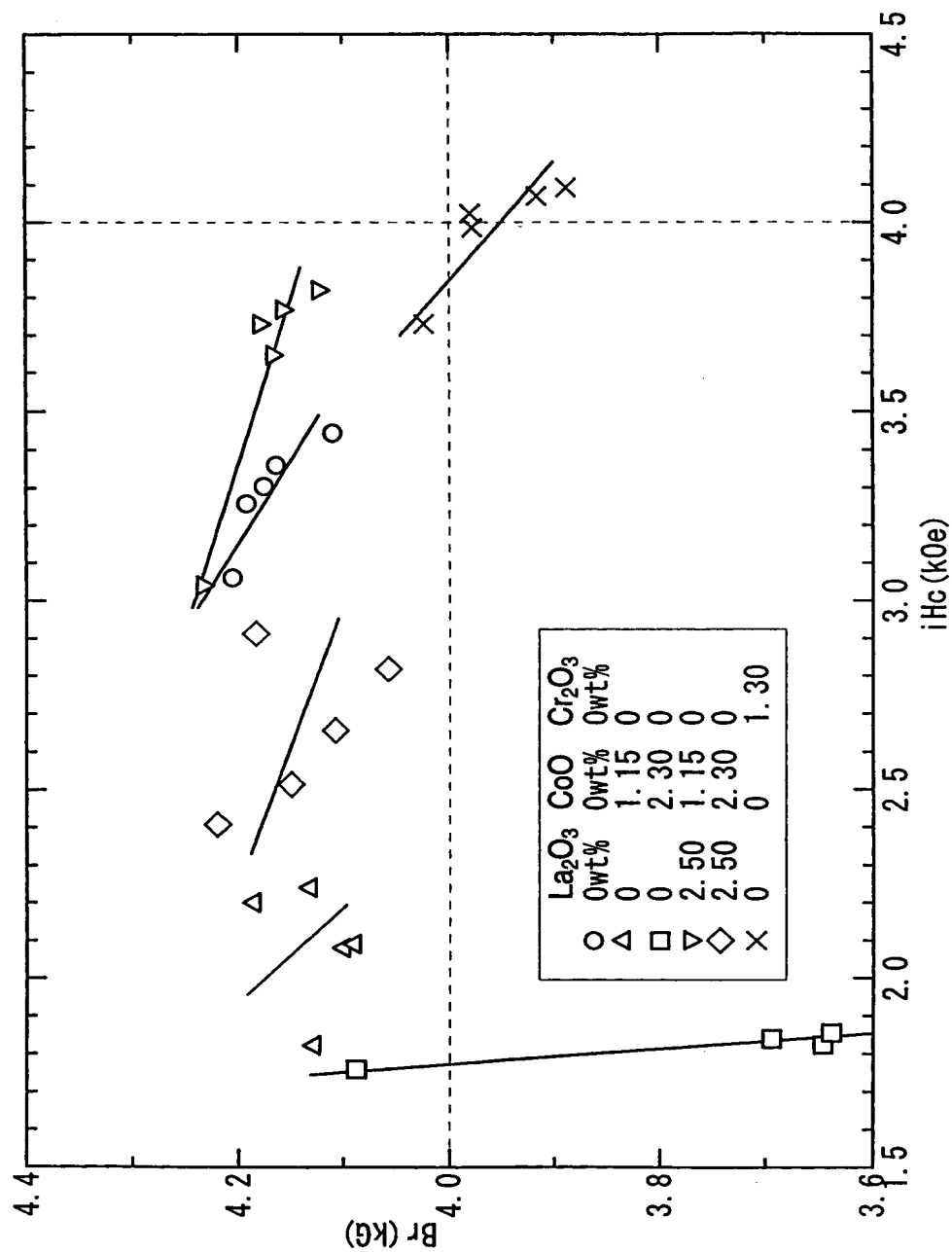
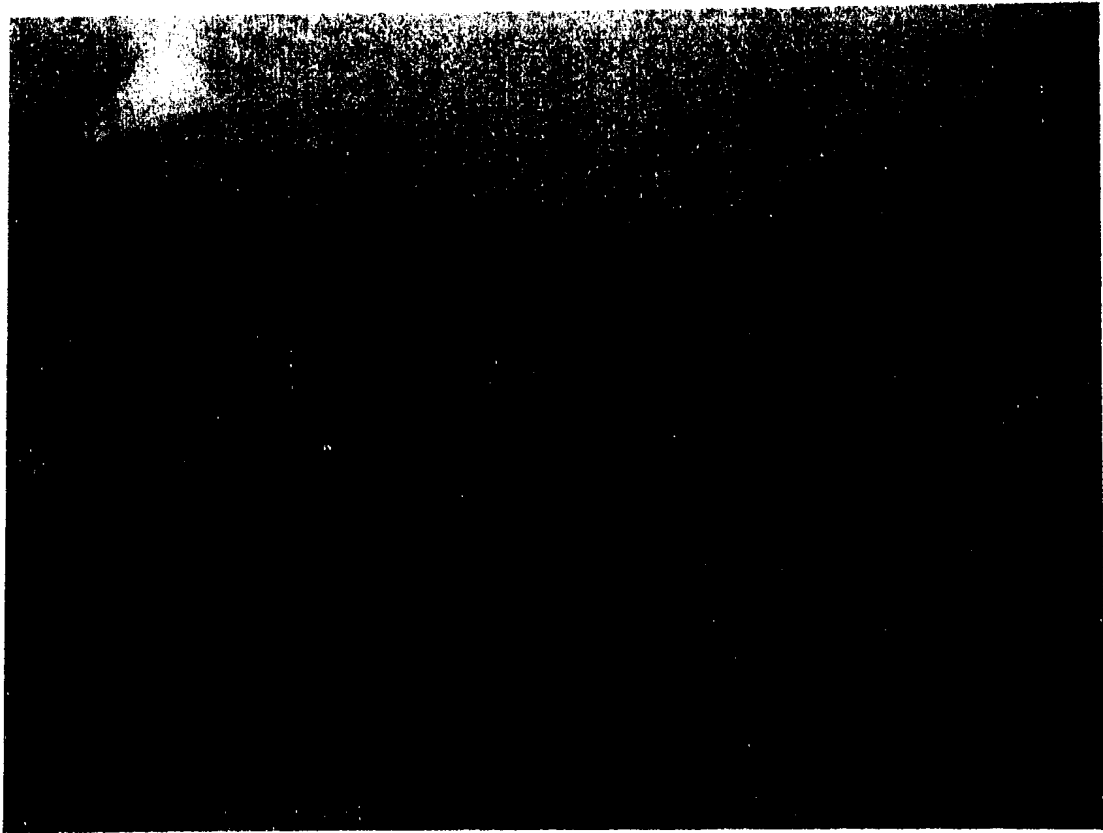


FIG. 9



100 nm

FIG. 10

